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A discrete solvent reaction field model for calculating molecular linear response properties in solution

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A discrete solvent reaction field model for calculating frequency-dependent molecular linear response properties of molecules in solution is presented. The model combines a time-dependent density functional theory (QM) description of the solute molecule with a classical (MM) description of the discrete solvent molecules. The classical solvent molecules are represented using distributed atomic charges and polarizabilities. All the atomic parameters have been chosen so as to describe molecular gas phase properties of the solvent molecule, i.e., the atomic charges reproduce the molecular dipole moment and the atomic polarizabilities reproduce the molecular polarizability tensor using a modified dipole interaction model. The QM/MM interactions are introduced into the Kohn–Sham equations and all interactions are solved self-consistently, thereby allowing for the solute to be polarized by the solvent. Furthermore, the inclusion of polarizabilities in the MM part allows for the solvent molecules to be polarized by the solute and by interactions with other solvent molecules. Initial applications of the model to calculate the vertical electronic excitation energies and frequency-dependent molecular polarizability of a water molecule in a cluster of 127 classical water molecules are presented. The effect of using different exchange correlation (xc)-potentials is investigated and the results are compared with results from wave function methods combined with a similar solvent model both at the correlated and uncorrelated level of theory. It is shown that accurate results in agreement with correlated wave function results can be obtained using xc-potentials with the correct asymptotic behavior. © 2003 American Institute of Physics.
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I. INTRODUCTION

The calculation of molecular properties of molecules in the condensed phase is a fundamental and important theoretical problem which still remains problematic. Since molecular properties like (hyper)polarizabilities are sensitive to the local environment an accurate calculation of these properties could serve as a test for the molecular models used in describing intermolecular forces. However, accurate calculation of molecular properties requires a quantum mechanical treatment which, due to high computational cost, is limited to small systems. Therefore the most successful methods divide the total system into the molecular system of interest which is treated with a quantum mechanical method and another part which contains the rest of the system which is treated by a much simpler method, usually a classical description.^{1–15}

Among these methods are the combined quantum mechanical and classical mechanics models (QM/MM).^{4–15} In the QM/MM method the solvent molecules are treated with a classical force field and the interactions between the solute and solvent are described with an effective operator, so the problem which remains is to find an accurate approximate representation of the solvent molecules and the solute–solvent interactions.¹⁶ The discrete representation of the solvent molecules requires a large number of solvent configurations over which the solute properties must be averaged.

This is typically done using Monte Carlo or MD techniques which lead to a large number of quantum mechanical calculations. For this reason the QM/MM method is often employed at a semiempirical level of theory.¹⁴

We have recently developed such a method which we denoted the discrete solvent reaction field model (DRF).¹⁷ In this model the QM part is treated using density functional theory (DFT). The solvent molecules (MM) are modeled by point charges representing the permanent electronic charge distribution, and distributed polarizabilities for describing the solvent polarization arising from many-body interactions. The QM/MM interactions are introduced into the Kohn–Sham equations and all interactions are solved self-consistently, thereby allowing for the solute to be polarized by the solvent. Furthermore, the inclusion of polarizabilities in the MM part allows for the solvent molecules to be polarized by the solute and by interactions with other solvent molecules. The advantage of including polarizabilities in the MM part is that all parameters can be obtained from gas phase properties. In general it is expected that a distributed polarizability approach will give better results than an approach using only a (anisotropic) polarizability located at a single site, especially as the size of the solvent molecule increases.¹⁸

The use of time-dependent density functional theory (TD-DFT) (Refs. 19–23) allows for the calculation of

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frequency-dependent response properties like electronic spectra and frequency-dependent polarizabilities. The use of TD-DFT for calculating molecular response properties in the gas-phase has been shown to be accurate especially using recently developed density functionals^{24–30} and the extension of TD-DFT to also treat molecules in solution is of great interest. So far the treatment of frequency-dependent response properties of molecules in solution within a TD-DFT approach has been done within the polarizable continuum model.^{31–33} Therefore, in this work we will include the discrete solvent reaction field model within the TD-DFT. This allows for the calculation of response properties of molecules in solution where the discrete representation of the solvent is retained and electron correlation of the QM part is included in an efficient manner. Within a QM/MM approach the treatment of frequency-dependent properties has been done using both correlated and uncorrelated wave function based methods.^{34–36} As in our previous study on dipole and quadrupole moments of water in aqueous solution¹⁷ we will adopt a single water structure for which there exists wave function QM/MM results.^{35,36} This will allow us to assess approximate exchange-correlation (xc) potentials for calculating molecular response properties in solution.

II. THEORY

A. The discrete reaction field model

In the QM/MM method the total (effective) Hamiltonian for the system is written as^{4–15}

$$\hat{H} = \hat{H}_{\text{QM}} + \hat{H}_{\text{QM/MM}} + \hat{H}_{\text{MM}}, \quad (1)$$

where \hat{H}_{QM} is the quantum mechanical Hamiltonian for the solute, $\hat{H}_{\text{QM/MM}}$ describes the interactions between solute and solvent and \hat{H}_{MM} describes the solvent–solvent interactions. The discrete reaction field model has been described in Ref. 17 within time-independent DFT. Here, the model will be extended to include the effect of an electric field at frequency, ω , perturbing the QM part.

Within the discrete reaction field model the QM/MM operator at a point r_i is given by

$$\hat{H}_{\text{QM/MM}} = \sum_i v^{\text{DRF}}(r_i, \omega) = \sum_i v^{\text{el}}(r_i) + \sum_i v^{\text{pol}}(r_i, \omega), \quad (2)$$

where the first term, v^{el} , is the electrostatic operator and describes the Coulombic interaction between the QM system and the permanent charge distribution of the solvent molecules. The second term, v^{pol} , is the polarization operator and describes the many-body polarization of the solvent molecules, i.e., the change in the charge distribution of the solvent molecules due to interaction with the QM part and other solvent molecules.

The charge distribution of the solvent is represented by atomic point charges, hence the electrostatic operator is given by

$$v^{\text{el}}(r_i) = \sum_s \frac{q_s}{R_{si}} = \sum_s q_s T_{si}^{(0)}, \quad (3)$$

where the zeroth order interaction tensor has been introduced and the index s runs over all atoms of the solvent molecules. In general the interaction tensor to a given order, n , can be written as

$$T_{pq, \alpha_1, \dots, \alpha_n}^{(n)} = \nabla_{pq, \alpha_1} \dots \nabla_{pq, \alpha_n} \left(\frac{1}{R_{pq}} \right), \quad (4)$$

where R_{pq} is the distance between the interacting entities.

The many-body polarization term is represented by induced atomic dipoles at the solvent molecules and the polarization operator is given by

$$v^{\text{pol}}(r_i, \omega) = \sum_s \mu_{s, \alpha}^{\text{ind}}(\omega) \frac{R_{si, \alpha}}{R_{si}^3} = - \sum_s \mu_{s, \alpha}^{\text{ind}}(\omega) T_{si, \alpha}^{(1)}, \quad (5)$$

where $R_{si, \alpha}$ is a component of the distance vector and $\mu_s^{\text{ind}}(\omega)$ is the induced dipole at site s . For Greek indices the Einstein summation convention is employed. The induced dipoles are discussed in more detail in the next section.

B. The frequency-dependent atomic induced dipoles

For a collection of atomic polarizabilities in an electric field, assuming linear response, the induced atomic dipole at site s is given by

$$\mu_{s, \alpha}^{\text{ind}}(\omega) = \alpha_{s, \alpha \beta} \left[F_{s, \beta}^{\text{init}}(\omega) + \sum_{t \neq s} T_{st, \beta \gamma}^{(2)} \mu_{t, \gamma}^{\text{ind}}(\omega) \right], \quad (6)$$

where $\alpha_{s, \alpha \beta}$ is a component of the atomic polarizability tensor at site s , which for an isotropic atom gives $\alpha_{s, \alpha \beta} = \delta_{\alpha \beta} \alpha_s$. Here we neglect the frequency-dependence of the classical part, i.e., the atomic polarizability is frequency independent, but the model can easily be extended to include also this effect.^{37,38}

$F_{s, \beta}^{\text{init}}(\omega)$ is the initial electric field at site s and the last term is the electric field from the other induced dipoles. The dipole interaction tensor, $T_{st, \alpha \beta}^{(2)}$, is given by

$$T_{st, \alpha \beta}^{(2)} = \frac{3R_{st, \alpha} R_{st, \beta}}{R_{st}^5} - \frac{\delta_{\alpha \beta}}{R_{st}^3}. \quad (7)$$

The initial field in Eq. (6) is given as a sum of three terms,

$$F_{t, \beta}^{\text{init}}(\omega) = F_{t, \beta}^{\text{QM, el}}(\omega) + F_{t, \beta}^{\text{QM, nuc}} + F_{t, \beta}^{\text{MM, q}}, \quad (8)$$

where $F_{t, \beta}^{\text{QM, el}}(\omega)$ is the field arising from the frequency-dependent electronic charge distribution of the QM part,

$$F_{t, \beta}^{\text{QM, el}}(\omega) = - \int \rho(r_i, \omega) \frac{R_{it, \beta}}{R_{it}^3} dr_i = \int \rho(r_i, \omega) T_{it, \beta}^{(1)} dr_i \quad (9)$$

and $F_{t, \beta}^{\text{QM, nuc}}$ is the field arising from the QM nuclei,

$$F_{t, \beta}^{\text{QM, nuc}} = \sum_m \frac{Z_m R_{mt, \beta}}{R_{mt}^3} = - \sum_m Z_m T_{mt, \beta}^{(1)} \quad (10)$$

and $F_{t, \beta}^{\text{MM, q}}$ is the field arising from the point charges at the solvent molecules,

$$F_{t, \beta}^{\text{MM, q}} = \sum_s' \frac{q_s R_{st, \beta}}{R_{st}^3} = - \sum_s' q_s T_{st, \beta}^{(1)}. \quad (11)$$

The prime in Eq. (11) indicates that the sum is restricted to sites which do not belong to the same molecule.

The initial field in Eq. (8) does not include the electric field perturbing the QM part which means that the field perturbing the QM part is in fact the local field felt by the QM molecule. The reason for this approach is that we are interested in obtaining the properties of a single molecule in solution. This method leads to the identification of the calculated properties as the solute properties, i.e., the polarizability of the solute including the solvent effects but not corrected for the difference between the local field and the macroscopic field. For a discussion of these effects and corrections within the dielectric continuum model see, e.g., Refs. 39–41.

Since the induced dipole in Eq. (6) depends on the induced dipoles at the other sites these equations have to be solved self-consistently. This can be done analytically by rewriting the equations into a $3N \times 3N$ linear matrix equation, with N the number of atoms, as^{42,43}

$$A\mu^{\text{ind}}(\omega) = F^{\text{init}}(\omega) \quad (12)$$

and the components of the matrix, $A_{st,\alpha\beta}$, given by

$$A_{st,\alpha\beta} = (\alpha_{s,\alpha\beta}^{-1} \delta_{st} - T_{st,\alpha\beta}^{(2)}). \quad (13)$$

This matrix equation can then be solved for the induced dipoles using standard mathematical tools for solving linear equations. The inverse of the matrix A , the so called relay matrix B , is a generalized polarizability matrix which describes the total linear response of the discrete solvent molecules.

It is well known that if the distance between two polarizable points becomes too small the induced dipoles will grow towards infinity. In order to avoid this “polarizability catastrophe” Thole⁴⁴ modified the dipole interaction tensor using smeared-out dipoles. The screened dipole interaction tensor can be written as

$$T_{pq,\alpha\beta}^{(2)} = \frac{3f_{pq}^T R_{pq,\alpha} R_{pq,\beta}}{R_{pq}^5} - \frac{f_{pq}^E \delta_{\alpha\beta}}{R_{pq}^3}, \quad (14)$$

where the damping functions f_{pq}^T and f_{pq}^E have been introduced. If we consider an exponential decaying charge distribution the screening functions in Eq. (14) are given by⁴⁵

$$f_{pg}^E = 1 - [1 + s_{pq} + \frac{1}{2}s_{pq}^2] \exp(-s_{pq})$$

and

$$f_{pg}^T = f_{pg}^E - \frac{1}{6}s_{pq}^3 \exp(-s_{pq}), \quad (15)$$

where the term s_{pq} is given by $s_{pq} = aR_{pq}/(\alpha_p\alpha_q)^{1/6}$, with a the screening length, and α_p the atomic polarizability of atom p .

C. The time-dependent Kohn–Sham equation

If one is interested in time-dependent properties within DFT one has to resort to the time-dependent Kohn–Sham equations,^{19–23}

$$i \frac{\partial}{\partial t} \phi_i(r, t) = \left[-\frac{1}{2} \nabla^2 + v_{\text{eff}}(r, t) \right] \phi_i(r, t), \quad (16)$$

with the effective potential given by

$$v_{\text{eff}}(r, t) = \int dr' \frac{\rho(r', t)}{|r - r'|} + v^{\text{per}}(t) + v^{\text{DRF}}(r, t) + v_{\text{xc}}(r, t), \quad (17)$$

where $v^{\text{DRF}}(r, t)$ is the operator defined in Eq. (2) and $v^{\text{per}}(t)$ is the perturbing field turned on slowly in the distant past. The last term is the time-dependent xc-potential which in the adiabatic approximation is given by the functional derivative of the xc-energy

$$v_{\text{xc}}[\rho](r, t) \approx \frac{\delta E_{\text{xc}}[\rho_t]}{\delta \rho_t(r)} = v_{\text{xc}}[\rho_t](r). \quad (18)$$

The time-dependent electronic density is given by

$$\rho(r, t) = \sum_i^{\text{occ}} n_i |\phi_i(r, t)|^2, \quad (19)$$

where n_i is the occupation number of orbital i .

D. Linear response of the density matrix

Since we are interested in linear response properties we look at the first-order change in the density to a time-dependent perturbation,

$$\begin{aligned} \delta\rho(r, \omega) &= \sum_{s,t} P_{st}(\omega) \phi_s(r) \phi_t^*(r) \\ &= \sum_{i,a} P_{ia}(\omega) \phi_i(r) \phi_a^*(r) + P_{ai}(\omega) \phi_a(r) \phi_i^*(r), \end{aligned} \quad (20)$$

where P is the first-order density matrix and a, b indicates virtual orbitals, i, j occupied orbitals, and s, t indicates general orbitals. By expanding the KS-equations to first-order in the perturbing potential we find that the first-order density matrix is given by

$$P_{st}(\omega) = \frac{\Delta n_{st}}{(\epsilon_s - \epsilon_t)\omega} \delta v_{st}^{\text{eff}}(\omega), \quad (21)$$

where Δn_{st} is the difference in occupation numbers, i.e., 1 for $st=ai$ and -1 for $st=ia$. The change in the effective potential, $\delta v_{st}^{\text{eff}}$, is dependent on the first order change in the density and is given by

$$\begin{aligned} \delta v_{st}^{\text{eff}}(\omega) &= \delta v_{st}^{\text{per}}(\omega) + \delta v_{st}^{\text{scf}}(\omega) \\ &= \delta v_{st}^{\text{per}}(\omega) + \int dr' \phi_s^*(r) \left[\int dr' \frac{\delta\rho(r', \omega)}{|r - r'|} \right. \\ &\quad \left. + v_{\text{xc}}[\delta\rho](r, \omega) + v^{\text{DRF}}[\delta\rho](r, \omega) \right] \phi_t(r), \end{aligned} \quad (22)$$

where the self-consistent field, δv^{scf} , denotes terms which depend on the first-order change in the density. The contribution from the DRF operator is given by

$$\begin{aligned}
v^{\text{DRF}}[\delta\rho](r_i, \omega) &= - \sum_s \mu_{s,\alpha}^{\text{ind}}[\delta\rho](\omega) T_{si,\alpha}^{(1)} \\
&= - \sum_s \sum_t B_{st,\alpha\beta} F_{s,\beta}^{\text{qm.el}}[\delta\rho](\omega) T_{si,\alpha}^{(1)} \\
&= - \sum_s \sum_t B_{st,\alpha\beta} \int \delta\rho(r_j, \omega) T_{js,\beta}^{(1)} dr_j T_{si,\alpha}^{(1)}, \quad (23)
\end{aligned}$$

where B is the relay matrix. The DRF contribution arises from the induced dipoles in the MM part due to the first-order change in the QM charge distribution. Inserting the first order change in the density, Eq. (20) into Eq. (22) allows for the change in the effective potential to be written as

$$\delta v_{st}^{\text{eff}}(\omega) = \delta v_{st}^{\text{per}}(\omega) + \sum_{uv} K_{st,uv} P_{uv}(\omega), \quad (24)$$

where the coupling matrix, \mathbf{K} , has been introduced. The coupling matrix will be described in more detail later. Inserting Eq. (24) into Eq. (21) the first-order density matrix can be written as

$$P_{st}(\omega) = \frac{\Delta n_{st}}{(\epsilon_s - \epsilon_t)\omega} \left[\delta v_{st}^{\text{per}}(\omega) + \sum_{uv} K_{st,uv} P_{uv}(\omega) \right]. \quad (25)$$

This can be written as a set of coupled linear equations for the first-order density matrix elements using the fact that only elements relating occupied and virtual orbitals are non-zero,

$$\begin{aligned}
\sum_{jb} [\delta_{ij} \delta_{ab} (\epsilon_a - \epsilon_i + \omega) + K_{ia,jb}] P_{jb} + \sum_{jb} K_{ia,bj} P_{bj} \\
= -(\delta v_{ia}^{\text{per}}), \quad (26)
\end{aligned}$$

$$\begin{aligned}
\sum_{jb} [\delta_{ij} \delta_{ab} (\epsilon_a - \epsilon_i - \omega) + K_{ai,bj}] P_{bj} + \sum_{jb} K_{ai,jb} P_{jb} \\
= -(\delta v_{ai}^{\text{per}}). \quad (27)
\end{aligned}$$

These equations can be written as one matrix equation using the more common notation $X_{jb} = P_{jb}$ and $Y_{jb} = P_{bj}$ as

$$\left[\begin{pmatrix} \mathbf{A} & \mathbf{C} \\ \mathbf{C}^* & \mathbf{A}^* \end{pmatrix} - \omega \begin{pmatrix} -\mathbf{1} & \mathbf{0} \\ \mathbf{0} & \mathbf{1} \end{pmatrix} \right] \begin{pmatrix} X \\ Y \end{pmatrix} = - \begin{pmatrix} \delta v^{\text{per}} \\ \delta v^{\text{per}*} \end{pmatrix}, \quad (28)$$

where the individual matrix elements are defined as

$$A_{ia,jb} = \delta_{ab} \delta_{ij} (\epsilon_a - \epsilon_i) + K_{ia,jb} \quad (29)$$

and

$$C_{ia,jb} = K_{ia,bj}. \quad (30)$$

In the TD-DFT the equality $K_{ia,jb} = K_{ia,bj}$ allows for the equations to be reduced to half the size which is not the case in the TD-HF where this equality is not valid. From the solution of the linear equations in Eq. (28) we have access to the frequency-dependent polarizability or by transforming the left-hand side into an eigenvalue equation we can obtain the excitation energies and oscillator strengths.

E. The coupling matrix

The coupling matrix describes the linear response of the self-consistent field to changes in the density and consists of three terms,

$$K_{st,uv} = \frac{\partial v_{st}^{\text{scf}}}{\partial P_{uv}} = K_{st,uv}^{\text{Coul}} + K_{st,uv}^{\text{xc}} + K_{st,uv}^{\text{DRF}}. \quad (31)$$

The first term is the Coulomb part given by

$$K_{st,uv}^{\text{Coul}} = \int \int dr_i dr_j \phi_s^*(r_i) \phi_t(r_i) \frac{1}{|r_i - r_j|} \phi_u(r_j) \phi_v^*(r_j), \quad (32)$$

the second term is the xc part,

$$K_{st,uv}^{\text{xc}} = \int \int dr_i dr_j \phi_s^*(r_i) \phi_t(r_i) \frac{\delta v_{\text{xc}}(r_i, \omega)}{\delta \rho(r_j, \omega)} \phi_u(r_j) \phi_v^*(r_j), \quad (33)$$

and the last term is the DRF part,

$$K_{st,uv}^{\text{DRF}} = \int dr_i \phi_s^*(r_i) \phi_t(r_i) \frac{\partial v^{\text{DRF}}(r_i, \omega)}{\partial P_{uv}} \quad (34)$$

$$\begin{aligned}
&= - \int dr_i \phi_s^*(r_i) \phi_t(r_i) \sum_s \sum_t B_{st,\alpha\beta} T_{js,\beta}^{(1)} T_{si,\alpha}^{(1)} \\
&\quad \times \frac{\partial \delta \rho(r_j, \omega)}{\partial P_{uv}} \quad (35)
\end{aligned}$$

$$\begin{aligned}
&= - \int \int dr_i dr_j \phi_s^*(r_i) \phi_t(r_i) \sum_s \sum_t B_{st,\alpha\beta} \\
&\quad \times T_{js,\beta}^{(1)} T_{si,\alpha}^{(1)} \phi_u^*(r_j) \phi_v(r_j). \quad (36)
\end{aligned}$$

F. Implementation

The DRF model has been implemented into a local version of the Amsterdam Density Functional (ADF) program package.^{46,47} The extension to the TD-DFT part has been implemented into the RESPONSE module of the ADF.^{48–50} In the RESPONSE module the functional derivative of the xc-potential in Eq. (33) is restricted to the adiabatic LDA (ALDA) xc-potential. The coupling matrix in Eq. (28) becomes very big for large systems and for this reason this matrix is not constructed but the linear equations in Eq. (28) are solved iteratively, for details see Ref. 48. This means that the DRF response operator, Eq. (23) is never calculated by constructing the relay matrix, B , but the induced dipole moments due to the first-order change in the charge distribution are calculated by solving a set of linear equations like in Eq. (12).

In ADF the KS equations and the linear response equations are solved by numerical integration which means that the DRF operator has to be evaluated in each integration point. Since the numerical integration grid is chosen on the basis of the quantum part alone care must be taken when evaluating the DRF operator if the integration points are close to a classical atom. In order to avoid numerical instabilities we introduce a damping of the operator at small distances which is modeled by modifying the distance R_{ij} to obtain a scaled distance S_{ij} ,³⁸

TABLE I. Even-tempered basis set for the H, O atoms (in parentheses the number n of $1s$, $2p$, $3d$, $4f$) with the orbital exponent $\zeta = \alpha\beta^i$, $i = 1, \dots, n$, $\beta = 1.7$. The value of α for the most diffuse $1s$, $2p$, $3d$, and $4f$ is presented.

Atom	$1s$	$2p$	$3d$	$4f$
H($4s3p3d$)	0.282 564	0.451 156	0.407 083	
O($8s6p3d4f$)	0.181 199	0.238 632	0.530 772	0.359 191

$$S_{ij} = v_{ij} R_{ij} = f(R_{ij}), \quad (37)$$

where v_{ij} is a scaling factor and $f(R_{ij})$ an appropriately chosen function of R_{ij} . Furthermore, each component of R_{ij} is also scaled by v_{ij} , so the reduced distance becomes,

$$S_{ij} = \sqrt{S_{ij,\alpha} S_{ij,\alpha}} = v_{ij} \sqrt{R_{ij,\alpha} R_{ij,\alpha}} = v_{ij} R_{ij}, \quad (38)$$

consistent with the definition in Eq. (37). The damped operator can thus be obtained by modifying the interaction tensors in Eqs. (3), (5), and (23),

$$T_{ij,\alpha_1, \dots, \alpha_n}^{(n)} = \nabla_{\alpha_1} \cdots \nabla_{\alpha_n} \left(\frac{1}{S_{ij}} \right), \quad (39)$$

which is equivalent to replacing R_{ij} by S_{ij} and $R_{ij,\alpha}$ by $S_{ij,\alpha}$ in the regular formulas for the interaction tensors. The particular form of the scaling function employed here is³⁸

$$f(r_{pq}) = \frac{r_{pq}}{\text{erf}(r_{pq})}, \quad (40)$$

which was obtained by considering the interaction between two Gaussian charge distributions with unity exponents.

III. COMPUTATIONAL DETAILS

In this work we use a large even-tempered basis set of Slater-type orbitals with orbital exponent $\zeta = \alpha\beta^i$, $i = 1, \dots, n$; the details of the basis set are presented in Table I. We tested different xc potentials, the local density approximation (LDA), Becke–Lee–Yang–Parr (BLYP),^{51,52} the Becke–Perdew (BP),^{51,53} the van Leeuwen–Baerends (LB94),⁵⁴ the statistical averaging of (model) orbital potentials (SAOP),^{27,55,56} and the gradient-regulated asymptotic connection procedure applied to the BP potentials (BP-GRAC).^{29,30} The BLYP and BP are examples of typical generalized gradient approximations (GGAs) potentials and the LB94 is an example of a so-called asymptotic correct potential due to the correct Coulombic decay of the potential at large distances. Whereas SAOP and BP-GRAC belong to a class of shape-corrected potentials which yield the correct asymptotic behavior. The BP-GRAC potential sets the HOMO level at the first ionization potential (IP) and therefore requires the IP as input. The SAOP xc-potential requires no additional input and the energy of the HOMO corresponds well with the IP.^{30,57} For this reason the IP needed as input for the BP-GRAC xc-potential is taken from the SAOP gas-phase calculation, i.e., IP = 0.45 a.u.

The parameters needed for the solvent molecules, i.e., point charges and atomic polarizabilities, were adopted from Ref. 17. The point charges are $q_H = 0.3345$ a.u. and $q_O = -0.6690$ a.u. which generate a molecular dipole moment

of 1.88 Debye. The atomic polarizabilities are $\alpha_H = 0.0690$ a.u. and $\alpha_O = 9.3005$ a.u. which reproduced the molecular polarizability tensor with a mean polarizability of 9.62 a.u. and a polarizability anisotropy of 0.52 a.u. The screening parameter, $a = 2.1304$, used in Eq. (15), was taken from Ref. 45.

The water structure we used in this work was taken from Ref. 58 and consists of 128 rigid water molecules where one molecule, the solute, is treated quantum mechanically. The total structure was obtained from a MD simulation using a polarizable force field⁵⁹ and the details about the simulation can be found in Refs. 35 and 36 but are summarized here for consistency. The average geometry is obtained from a simulation of a box containing 128 water molecules utilizing periodic boundary conditions with a spherical cutoff distance of 10.0 Å, temperature of 298 K, and a pressure of 0.103 MPa. After equilibration of the sample, the average geometry was obtained from a Boltzmann sampling of 8000 trajectories started from different initial velocity distributions and a simulations time of 20 ps for each trajectory. The intramolecular geometry of the water molecules was that in gas phase, i.e., $R_{O-H} = 0.9572$ Å and $\angle_{HOH} = 104.49^\circ$. The solute water molecule was placed in the xz -plane with the z -axis bisecting the H–O–H angle. Results obtained using this structure will be referred to as “liquid” phase results. We will perform one QM/MM calculation and therefore the molecular properties will not be averaged over different solvent configurations. However, the choice of this particular water structure allows for a direct comparison with results obtained from a similar model within a (multiconfigurational) self-consistent-field/molecular mechanics (MC-SCF/MM) (Ref. 35) or a coupled cluster/molecular mechanics (CC/MM) (Ref. 36) approach. Therefore, it is possible to make a detailed comparison between wave function methods and the DFT method for liquid phase calculations.

IV. RESULTS

A. Excitation energies

In Table II we present excitation energies, ω , and oscillator strengths, f , for the three lowest vertical singlet–singlet excitations of a water molecule in the gas phase calculated using different xc-potentials. The results are compared with results obtained from wave function methods, i.e., HF,³⁵ MC-SCF,³⁵ CCSD,³⁶ and experimental results taken from Ref. 60. From the results in Table II it is noted that LDA and the GGA potentials (BP and BLYP) underestimate the excitation energies considerably compared with the experimental results, i.e., for the first excitation ~ 1 eV, the second excitation ~ 1.5 eV, and for the third excitation as much as ~ 2 eV. The failure of these common xc-potentials to predict excitation energies for Rydberg-type states (for water the lowest excitations have a high degree of Rydberg character) has been identified as a result of the wrong asymptotic behavior of the xc-potentials.^{25,26} This is clearly illustrated by using the xc-functionals (LB94, SAOP, and BP-GRAC) with correct asymptotic behavior, for which the excitations energies are greatly improved compared with the experimental results. Especially the results obtained with the BP-GRAC

TABLE II. Excitation energies (ω) and oscillator strengths (f) of a water molecule in vacuum. ω in eV and f in a.u.

Method	${}^1A_1 \rightarrow {}^1B_1$		${}^1A_1 \rightarrow {}^1A_2$		${}^1A_1 \rightarrow 2\ {}^1A_1$	
	ω	f	ω	f	ω	f
LDA	6.47	0.04	7.55	...	7.76	0.00006
BLYP	6.24	0.04	7.33	...	7.53	0.0002
BP	6.57	0.04	7.50	...	7.67	0.00006
LB94	7.89	0.04	9.68	...	9.91	0.09
SAOP	7.72	0.05	9.53	...	9.68	0.09
BP-GRAC	7.33	0.05	9.15	...	9.48	0.09
HF ^a	8.65	...	10.3
MC-SCF ^a	7.85	...	9.56
CCSD ^b	7.62	0.05	9.38	...	9.88	0.06
Expt. ^c	7.4	...	9.1	...	9.7	...

^aResults from Ref. 35 using the aug-cc-pVQZ basis set.^bResults from Ref. 36 using the d-aug-cc-pVTZ basis set.^cResults taken from Ref. 60.

xc-potentials are in good agreement with the experimental results. Comparing with the wave function results we see that HF overestimates the excitation energies compared with the experiments but the MC-SCF and CCSD results are in good agreement with experiment and also with the calculations performed with the asymptotic correct xc-potentials.

The excitation energies and oscillator strengths for a water molecule in a cluster of 127 classical water molecules calculated using the different xc-functional are presented in Table III. The results are compared with results for the same water cluster obtained using the HF/MM,³⁵ MC-SCF/MM,³⁵ and CCSD/MM (Ref. 36) method. Also presented in Table III is the solvation shift, $\Delta\omega$, i.e., the shift in the excitation energies in going from the gas-phase to the “liquid” phase. Comparing results using LDA with the GGA’s (BLYP and BP) results we find good agreement for excitation energies, oscillator strengths, and solvation shifts which were also observed for the gas-phase results. Furthermore, comparing the results using the asymptotic correct xc-potentials we also find a good agreement between the results, especially those obtained using SAOP and BP-GRAC. Comparing the LDA/GGA results with the results from the asymptotic correct xc-potentials we find that the agreement is less good than in the gas-phase. For the first two excitations the excitation en-

ergy is underestimated considerably and more than in the gas-phase leading to a solvation shift that is too small. For the third excitation the excitation energy is still underestimated but the solvation shift is overestimated. Using LDA/GGA this excitation was actually identified lying above other excitations which was not the case for the asymptotic correct xc-potentials. This excitation has a strong Rydberg character and is therefore very sensitive to the asymptotic part of the xc-potential. Comparing the results from the asymptotic correct xc-potentials with the wave function results we find that the excitation energies obtained with HF/MM are smaller but there is a good agreement with both the MC-SCF/MM and the CCSD/MM results. If we look at the solvent shift for the three excitations we see that both the wave function methods and DFT (except using LDA/GGA) predict that the excitations are shifted by approximately the same amount, i.e., that the three excitation energies are perturbed by the solvent in the same manner. Also, if we look at the oscillator strengths for the three excitations the first and third excitation are stronger than the second excitation. In the gas phase the second excitation is dipole forbidden. Also, comparing the second and third excitation energy we find, both in the gas phase and in the “liquid” phase, that DFT predicts a smaller difference compared with CCSD.

TABLE III. Excitation energies (ω), solvation shift ($\Delta\omega$), and oscillator strengths (f) for a water molecule in a cluster of 127 classical water molecules. ω and $\Delta\omega$ in eV and f in a.u.

Method	${}^1A_1 \rightarrow {}^1B_1$			${}^1A_1 \rightarrow {}^1A_2$			${}^1A_1 \rightarrow 2\ {}^1A_1$		
	ω	$\Delta\omega$	f	ω	$\Delta\omega$	f	ω	$\Delta\omega$	f
LDA/DRF	6.75	0.28	0.051	7.72	0.17	0.008	8.93	1.17	0.060
BLYP/DRF	6.49	0.25	0.055	7.48	0.15	0.009	8.71	1.18	0.063
BP/DRF	6.80	0.23	0.045	7.64	0.14	0.008	9.03	1.36	0.050
LB94/DRF	8.57	0.68	0.070	10.56	0.88	0.001	10.62	0.71	0.116
SAOP/DRF	8.25	0.53	0.075	10.18	0.65	0.003	10.27	0.59	0.112
BP-GRAC/DRF	8.09	0.76	0.084	10.12	0.97	0.003	10.31	0.83	0.118
HF/MM ^a	9.49	0.84	...	11.3	1.0
MC-SCF/MM ^a	8.62	0.77	...	10.5	0.9
CCSD/MM ^b	8.18	0.56	0.079	9.97	0.60	0.006	10.56	0.68	0.113

^aResults from Ref. 35 using the aug-cc-pVQZ basis set.^bResults from Ref. 36 using the d-aug-cc-pVTZ basis set.

TABLE IV. Frequency-dependent polarizability of a water molecule in vacuum. Frequency (ω) and polarizability in a.u.

	ω	LDA	BLYP	BP	LB94	SAOP	BP-GRAC	HF ^a	MC-SCF ^b	CCSD ^c	Expt. ^d
α_{xx}	0.0000	10.59	10.87	10.35	9.89	9.88	10.12	9.18	9.74	9.94 (9.98)	...
	0.0428	10.65	10.93	10.41	9.94	9.93	10.17	...	9.79	9.99	...
	0.0570	10.70	10.98	10.45	9.978	9.97	10.21	...	9.82	10.03	...
	0.0856	10.84	11.13	10.59	10.08	10.08	10.33	...	9.92	10.13	10.31
α_{yy}	0.0000	10.65	11.06	10.30	8.57	8.92	9.68	7.90	9.15	9.05 (9.35)	...
	0.0428	10.78	11.21	10.42	8.63	8.99	9.77	...	9.21	9.13	...
	0.0570	10.88	11.33	10.52	8.68	9.05	9.84	...	9.28	9.19	...
	0.0856	11.21	11.72	10.82	8.84	9.23	10.07	...	9.45	9.37	9.55
α_{zz}	0.0000	10.60	10.88	10.28	9.30	9.52	9.91	8.52	9.36	9.40 (9.61)	...
	0.0428	10.68	10.97	10.36	9.36	9.58	9.98	...	9.41	9.45	...
	0.0570	10.75	11.05	10.42	9.40	9.63	10.03	...	9.46	9.50	...
	0.0856	10.95	11.27	10.61	9.53	9.76	10.19	...	9.58	9.63	9.91
$\bar{\alpha}$	0.0000	10.61	10.94	10.31	9.25	9.44	9.90	8.53	9.42	9.47 (9.65)	9.83 ^e
	0.0428	10.70	11.04	10.40	9.31	9.50	9.97	...	9.47	9.52	...
	0.0570	10.78	11.12	10.46	9.35	9.55	10.03	...	9.52	9.57	...
	0.0856	11.00	11.37	10.67	9.48	9.69	10.20	...	9.65	9.71	9.92
$\Delta\alpha$	0.0000	0.05	0.19	0.06	1.14	0.84	0.38	1.11	0.43	0.78 (0.54)	...
	0.0428	0.11	0.26	0.06	1.13	0.82	0.34	...	0.41	0.76	...
	0.0570	0.16	0.33	0.08	1.12	0.80	0.32	...	0.39	0.74	...
	0.0856	0.33	0.53	0.22	1.08	0.75	0.22	...	0.34	0.67	0.67

^aResults taken from Ref. 66.^bResults taken from Ref. 35 using the aug-cc-pVQC.^cResults taken from Ref. 36 using the aug-cc-pVTZ basis set. In parentheses results taken from Ref. 67 using the d-aug-cc-pVTZ basis set.^dResults from Ref 68 at $\omega=0.088$ a.u. ($\lambda=514.5$ nm).^eResults taken from Ref. 69.

In the experimental absorption spectrum of liquid water two absorption peaks are found.^{61,62} The first peak has a maximum ~ 8.2 eV ($\Delta\omega \sim 0.8$ eV) and the second peak ~ 9.9 eV ($\Delta\omega \sim 0.2$ eV). The shifts of the excitation found in ice are even larger, i.e., the first maximum ~ 8.5 eV ($\Delta\omega \sim 1.1$ eV) and a broad shoulder ~ 10.4 eV ($\Delta\omega \sim 0.7$ eV).^{62,63} The first peak is assigned to the $^1A_1 \rightarrow 1^1B_1$ (first) excitation and the second peak to $^1A_1 \rightarrow 2^1A_1$ (third) excitation. Comparing the liquid results with the calculated results we find a good agreement for the first excitation both for the excitation energy and for the solvent shift, especially using BP-GRAC. For the third excitation the solvent shift is found experimentally to be much smaller than the calculated shift. As indicated, experimentally the shifts in the two excitations depend on whether the condensed phase is liquid water or ice. This indicates that the solvent shift for the two excitations could behave differently with respect to the local environment of the solvent. Therefore, it could be important to include a more appropriate sampling of the local structure of the solvent, i.e., using a larger number of solvent configurations than the average structure used in this work. This will also provide line broadening of the excitations due to the fluctuations in the local environment of the solvent. However, it should be mentioned also that other effects can account for the difference, e.g., in this approach we neglect the short-range repulsion between water molecules. Also, the solvent effects are introduced as a mean field theory, i.e., the solvent feels the mean field from the QM electrons (see, e.g., Refs. 5, 64, 65).

B. Frequency-dependent polarizability

In Table IV we present the static and frequency-dependent polarizability for a single water molecule at frequencies $\omega=0.0428, 0.0570, 0.0856$ a.u. ($\lambda=1064, 800, 532$ nm, respectively) calculated using different xc-potentials. The results are compared with HF,⁶⁶ MC-SCF,³⁵ CCSD,^{36,67} and experimental results.⁶⁸ Also presented is the mean polarizability, $\bar{\alpha}$, defined as

$$\bar{\alpha} = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}), \quad (41)$$

and the polarizability anisotropy, $\Delta\alpha$, as

$$\Delta\alpha = \sqrt{\frac{1}{2}[(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{xx} - \alpha_{zz})^2 + (\alpha_{yy} - \alpha_{zz})^2]}. \quad (42)$$

From the results in Table IV we see that the LDA/GGA results are larger than the results obtained with the asymptotic correct xc-potentials. Also, the size of the individual components of the polarizability tensor are nearly identical with LDA/GGA resulting in an anisotropy which is much smaller than that obtained with the asymptotic correct xc-potentials. The frequency dispersion is also found to be larger with LDA/GGA for the components and mean polarizability. However, for the frequency dispersion for the anisotropy we find the LDA/GGA predicts an increase in the anisotropy with increasing frequency whereas the asymptotic corrects xc-potentials predicts a decrease. Comparing the results from the three asymptotic correct xc-potentials we find that BP-GRAC predicts the largest components and mean

TABLE V. Frequency-dependent polarizability of a water molecule in a cluster of 127 classical water molecules. Frequency (ω) and polarizability in a.u.

	ω	LDA	BLYP	BP	LB94	SAOP	BP-GRAC	MC-SCF ^a	CCSD ^b
α_{xx}	0.0000	10.51	10.79	10.25	9.79	9.80	9.91	9.54	9.66 (9.77)
	0.0428	10.57	10.85	10.31	9.84	9.84	9.96	9.58	9.70 (9.82)
	0.0570	10.61	10.90	10.35	9.88	9.88	10.00	9.62	9.74 (9.85)
	0.0856	10.75	11.05	10.48	9.98	9.99	10.11	9.71	9.83 (9.96)
α_{yy}	0.0000	11.55	12.09	11.21	9.14	9.55	10.27	9.72	9.62 (10.01)
	0.0428	11.69	12.26	11.35	9.21	9.63	10.36	9.80	9.70 (10.10)
	0.0570	11.81	12.40	11.46	9.27	9.69	10.44	9.86	9.76 (10.17)
	0.0856	12.17	12.83	11.79	9.43	9.89	10.67	10.0	9.96 (10.39)
α_{zz}	0.0000	10.93	11.28	10.64	9.63	9.85	10.15	9.82	9.82 (10.13)
	0.0428	11.02	11.37	10.72	9.69	9.91	10.21	9.88	9.88 (10.19)
	0.0570	11.08	11.45	10.78	9.73	9.96	10.26	9.92	9.92 (10.24)
	0.0856	11.28	11.66	10.96	9.86	10.10	10.41	10.0	10.05 (10.38)
$\bar{\alpha}$	0.0000	11.00	11.39	10.70	9.52	9.73	10.11	9.70	9.70 (9.97)
	0.0428	11.09	11.50	10.79	9.58	9.79	10.18	9.75	9.76 (10.04)
	0.0570	11.17	11.58	10.86	9.62	9.84	10.23	9.80	9.91 (10.09)
	0.0856	11.40	11.85	11.08	9.75	9.99	10.40	9.93	9.95 (10.24)
$\Delta\alpha$	0.0000	0.90	1.14	0.84	0.59	0.28	0.31	0.25	0.18 (0.32)
	0.0428	0.98	1.24	0.91	0.57	0.26	0.35	0.27	0.18 (0.33)
	0.0570	1.04	1.32	0.97	0.55	0.24	0.39	0.27	0.17 (0.36)
	0.0856	1.25	1.57	1.15	0.50	0.19	0.49	0.29	0.19 (0.43)

^aResults from Ref. 35 using the aug-cc-pVQC basis set.^bResults from Ref. 36 using the aug-cc-pVTZ basis set. In parentheses results using the d-aug-cc-pVTZ basis set.

polarizability but the smallest anisotropy. LB94 predicts the largest anisotropy of the functionals due to a small yy component. Comparing with the wave function results we find that SAOP is in good agreement with MC-SCF and CCSD. The static CCSD results using the d-aug-cc-pVTZ basis set⁶⁷ are in very good agreement with the CCSD(T) result.⁶⁶ Comparing with the static CCSD/d-aug-cc-pVTZ results we see that SAOP gives a slightly lower mean polarizability but a larger anisotropy due to a small yy component. The HF results for the components and anisotropy are the smallest whereas the anisotropy is among the largest. LB94 gives an improved result compared with HF but the yy component is still underestimated compared with CCSD/d-aug-cc-pVTZ and therefore gives a mean polarizability that is too low and high anisotropy that is too high. Comparing with the experimental results we see that the BP-GRAC results predict larger values, whereas all other results are lower than the experimental results. Since the experimental results also contain a contribution from zero-point vibrations (see Ref. 69 for an estimate of this contribution), a smaller theoretical value is expected.

The frequency-dependent polarizability for a single water molecule in a cluster of 127 classical water molecules calculated using different xc-potentials are presented in Table V. The results are calculated for the same frequencies as in the gas-phase and are compared with results for the same water cluster obtained with the MC-SCF/MM (Ref. 35) and CCSD/MM (Ref. 36) method. It should be mentioned that for the results in the cluster the off-diagonal components of the polarizability tensor are different from zero. These components are not presented since they will tend to zero if a careful averaging over different solvent configurations representing the isotropic liquid is performed. Since there is a

good correlation between the magnitude of the polarizability in the gas phase and in the liquid, i.e., LDA/GGA predict the largest values and MC-SCF the smallest, we will focus on trends for the shifts in the polarizability in going from gas-phase to the cluster. All methods predict a decrease in the yy component and an increase in the xx and zz components leading to an overall increase in the mean polarizability. However, the LDA/GGA methods predicts an increase in the anisotropy in contrast to the other methods. The reason for this is that LDA/GGA predict a shift of ~ 0.9 a.u. in the yy components, whereas the rest of the methods predict a shift of ~ 0.6 a.u. The shift in the zz component predicted with CCSD/d-aug-cc-pVTZ and MC-SCF is ~ 0.5 a.u., whereas the DFT methods predict a shift of ~ 0.3 a.u. If we compare the frequency dispersion in the anisotropy predicted with CCSD or MC-SCF we see an increase with increasing frequency; this is also found using BP-GRAC, whereas LB94 and SAOP predicts a decrease.

The polarizability of liquid water has also been considered in a few other studies.^{70–74} In general, the models^{70,73,74} which calculate the molecular polarizability by averaging over the polarizability obtained from different solvent configuration predicts a lowering of the mean polarizability in going from the gas-phase to the liquid phase. The models^{71,72} which, like in this work, first average the structure (or the electric field generated by the solvent) and then calculate the molecular polarizability, predict an increase in the mean polarizability in good agreement with the results of this work. This indicates that it is important to take the local fluctuation of the solvent structure into account when calculating the molecular properties.

An estimate of the frequency-dependent polarizability

can be obtained from the refractive index, $n(\omega)$, by using the Lorenz–Lorentz equation,⁴³

$$\bar{\alpha}(-\omega; \omega) = \frac{3M_w}{4\pi N_a \rho} \frac{n(\omega)^2 - 1}{n(\omega)^2 + 2}, \quad (43)$$

where M_w is the molecular weight, N_a is Avogadro's number, and ρ is the density. Using the refractive index of liquid water at $\omega = 0.0428$ a.u., $n(0.0428) = 1.326$,⁷⁵ and $\rho = 0.99707$ g/cm³ we obtain a polarizability of $\bar{\alpha} = 9.74$ a.u. This estimate is in very good agreement with the SAOP and MC-SCF results but in less good agreement with the CCSD or BP-GRAC results. If we instead use the refractive index at $\omega = 0.077$ a.u. ($\lambda = 589.32$ nm), $n = 1.33283$,⁷⁶ we obtain a polarizability of $\bar{\alpha} = 9.93$ a.u. again in good agreement with the SAOP and MC-SCF results at $\omega = 0.0856$ a.u. If we compare the liquid results at $\omega = 0.0428$ a.u. with the static results obtained in the gas phase we find a small decrease in the mean polarizability in going from the gas phase to the liquid phase even if we take the frequency dispersion into account.

V. CONCLUSIONS

We have in this work presented a discrete solvent reaction field model for calculating frequency-dependent molecular linear response properties of molecule in solution. The model combines a TD-DFT description of the solute molecule with a classical description of the discrete solvent molecules. The classical solvent molecules are represented using distributed atomic charges and atomic polarizabilities. All the atomic parameters have been chosen so as to describe molecular gas phase properties of the solvent molecule, i.e. atomic charges reproduce the molecular dipole moment and atomic polarizabilities reproduce the molecular polarizability tensor using Thole's modified dipole interaction model. As an initial application of the model we have calculated the vertical electronic excitation energies and frequency-dependent molecular (hyper)polarizability of a water molecule in a cluster of 127 classical water molecules. The effect of using different xc-potentials has been investigated and the results have been compared with the corresponding wave function results obtained using combined HF, MC-SCF or CCSD method with a similar solvent model. It was shown that accurate results in agreement with the CCSD and MC-SCF results could be obtained by using xc-potentials which have the correct asymptotic behavior. The use of the shape-corrected functionals like SAOP and BP-GRAC improved the results compared with the asymptotic correct LB94. However, the use of BP-GRAC requires the IP as input and the results are strongly dependent on the input value which therefore limits the usefulness of this functional.

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